AN EXPERIMENTAL DETERMINATION OF THE ABSOLUTE OSCILLATOR STRENGTHS OF SOME RESONANCE TRANSITIONS OF CHROMIUM AND NICKEL

Thesis by

Frank B. Estabrook

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1950

ACKNOWLEDGEMENTS

This research has been under the supervision of Professor R. B. King, to whom I wish to express my gratitude for his continued encouragement, guidance and aid. The experimental work was done in the laboratory of the Mount Wilson Observatory, all of whose facilities were most generously made available to me.

ABSTRACT

A brief account is given of the classical electron theory of anomalous dispersion and line absorption. The oscillator strength, or f-value, is introduced as the factor involved in taking over the results of classical theory in a modern quantum mechanical formulation. The relation between f-values and the transition probabilities of Einstein is derived.

A summary of methods for experimental determination of f-values for atomic transitions is given, and in particular the method of total absorption is considered in detail. The equivalent width or total absorption of an absorption line is defined, and the relation of this to the oscillator strength of the line, the so-called curve of growth, qualitatively explained.

The laboratory apparatus used in the present investigation is described in detail, as are the methods of obtaining and reducing the experimental data.

An account is given of unsuccessful experiments on the resonance lines of Ca. Absolute nf-values obtained for three lines of Cr are reported, and on the basis of unsatisfactory vapor pressure data, tentative absolute f-values for these lines are assigned. Absolute f-values for three lines of the Ni spectrum are reported, the vapor pressure data for Ni being reliable. A conversion factor is obtained by which the relative gf-values for Ni given by King may be reduced to an absolute scale.

TABLE OF CONTENTS

I. Introduction

The intensities of spectral lines from atomic and molecular sources have been studied occassionally in recent years, though the body of data relating to their wave-lengths is extremely more detailed and accurate. From a microscopic viewpoint, this situation means that the atomic energy levels have been located in considerable detail, and that atomic transition probabilities between these levels remain to a great extent unknown.

The practical difficulties of theoretical computation beset the latter as well as the former; hence transition probabilities are reliably known from theory only for a relatively small number of cases [1]. The determinations for heavy, complex elements in particular must be experimental.

In astronomy, the classification of stellar types is based principally on their characteristic spectra, which differ considerably both in the lines present and in the observed intensities of these lines. Thus, while the constituent elements of a star may be qualitatively determined from its spectrum, quantitative study of the intensities of lines in stellar spectra provides a tool for investigating the applicability of various stellar models, and hence for studying both the prevailing physical conditions and the relative abundances of various elements in stellar reversing layers. Basic to all such quantitative investigations must be information about the transition probabilities among the energy levels of the elements of astrophysical interest. Such information must be obtained primarily by investigations in the laboratory under carefully controlled conditions.

II. Transition Probabilities

The notion of a transition probability between two stationary states of an atom is perhaps best approached through the phenomenological theory of Einstein[2]. Briefly, if "u" refers to the level of higher energy, and "ℓ" to that of lower energy, we let $A_{\ell u}$ be the probability per unit time that an atom in the upper state will spontaneously "jump" to the lower, emitting a quantum of frequency ν. Planck's condition requires that

$$E_u - E_\ell = h\nu$$

where $E_u - E_\ell$ is the difference in energy of the two states. If u_ν is the electromagnetic energy density per unit frequency range present at the frequency ν, there will also be the possibility of absorption of a quantum $h\nu$ by an atom in the lower state. This probability per unit time per atom will be proportional to u_ν, and will be denoted by $u_\nu B_{u\ell}$. Einstein recognized that there must also be the inverse process of induced emission: that there will also be a probability per unit time that an atom in the upper state will be induced to jump to the lower (and emit a photon) by the presence of electromagnetic energy density u_ν. This latter we denote by $u_\nu B_{\ell u}$. By postulating detailed balance in the equilibrium of atoms and radiation at temperature T, relations between these transition probabilities may now be derived.

Under conditions of thermal equilibrium, the frequency distribution u_ν of electromagnetic radiation is known from Planck's radiation law. Also, from statistical theory, if N_o is the number of atoms per unit volume in the ground state (E = 0, unexcited), the number of

atoms per unit volume in a state of excitation energy E is given by $N_o(g/g_o)\exp(-E/kT)$. Here g is the statistical weight (2J + 1) of the state, and expresses the fact that this state is in reality a degenerate superposition of 2J + 1 simple states.

Therefore the equation of detailed balance becomes

$$g_l e^{-E_l/kT} u_\nu B_{ul} = g_u e^{-E_u/kT} u_\nu B_{lu} + g_u e^{-E_u/kT} A_{lu} \quad .$$

Substituting

$$u_\nu = \frac{8\pi h\nu^3}{c^3 (e^{h\nu/kT} - 1)} \quad ,$$

and requiring the result to be true for all T, we obtain

$$g_l B_{ul} = g_u B_{lu} = g_u A_{lu} \frac{c^3}{8\pi h\nu^3} \quad . \qquad (1)$$

III. Classical Theory of Dispersion and Absorption

Anomalous dispersion and line absorption are classically regarded as due to resonance effects of the bound electrons in a medium traversed by light. Considering such an electron as harmonically bound, subject to radiation losses, and forced into oscillation by the harmonic electric intensity $Ee^{i\omega t}$ of the radiation, we can write

$$\ddot{r} - \frac{2e^2}{3mc^3}\dddot{r} + \omega_o^2 r = \frac{e}{m} E e^{i\omega t} \qquad (2)$$

The amplitude and phase of the resulting steady-state vibration are then given by

$$r = \frac{e}{m} \frac{E}{\omega_o^2 - \omega^2 + i\gamma\omega}$$

This is a characteristic resonance curve of half-width $\gamma = \frac{2e^2\omega_o^2}{3mc^3}$ in angular frequency.

Here we might recognize that E is the field intensity acting to induce a dipole moment in the atom. If this atom is part of an isotropic polarizable medium, Lorentz has shown that the macroscopic E_o

which would be measured in the medium is given by

$$E_o = E - \frac{4\pi P}{3} ,$$

where P is the polarization, or dipole-moment per unit volume. That is

$$P = \mathcal{N} e r ,$$

where $\mathcal{N}$ is the number of such dipoles per unit volume. These relations then lead to the expression for complex index of refraction n :

$$\begin{aligned} n^2 &= 1 + 4\pi \frac{P}{E_o} \\ &= 1 + \frac{4\pi e^2 \mathcal{N}}{m} \frac{1}{\omega_o^2 - \omega^2 + i\gamma\omega - \frac{4\pi}{3}\frac{e^2\mathcal{N}}{m}} . \end{aligned} \tag{3}$$

Letting $n = \mu - ik$, where μ is interpreted as the ordinary index of refraction and $\frac{2\omega k}{c}$ enters in the exponential law of absorption for the medium; and further now assuming that $k \approx 0$ and $\mu - 1 \ll 1$ (which means, physically, a rarefied medium whose absorption is small), one can obtain the classical dispersion formula

$$\mu - 1 = \sum_r \frac{2\pi e^2}{m} \frac{\mathcal{N}_r}{\omega_r^2 - \omega^2} . \tag{4}$$

A summation has been introduced over the various resonances the atom possesses: each still characterized by an electron harmonically oscillating.

IV. Oscillator Strengths

The number $\mathcal{N}_r$ used above is, correctly, the number of harmonic oscillators (of angular frequency ω_r) per unit volume. This turns out not to be equal to the number of excited atoms per unit volume N, but rather we must set

$$\mathcal{N}_r = N f_r , \tag{5}$$

where f_r is called the oscillator strength of the transition giving rise to the spectral line $\lambda_r = \frac{2\pi c}{\omega_r}$. Thus equation (4) becomes

$$\mu - 1 = \sum_r \frac{2\pi e^2}{m} \frac{N f_r}{\omega_r^2 - \omega^2} \quad . \tag{6}$$

This result was verified in 1927 by Schrödinger and Heisenberg, using the full apparatus of wave mechanics; the expression for f_r in terms of the matrix elements for the transition is given in the Handbuch article of Bethe[3]. In astrophysical work it has become customary to use oscillator strengths rather than transition probabilities; hence we shall now give the connection between them.

V. The Relation Between f-values and the Einstein Coefficients[4]

In the neighborhood of a particular resonance ω_o of a rarefied medium for which $\mu - 1 \ll 1$, equation (3) may be separated to give

$$\begin{aligned} \mu - 1 &= \frac{2\pi N e^2}{m} \frac{\omega_o^2 - \omega^2}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2} \\ k &= \frac{2\pi N e^2}{m} \frac{\gamma \omega}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad . \end{aligned} \tag{7}$$

The equations of a monochromatic plane wave in this medium are

$$\begin{aligned} E_y &= a e^{-\frac{\omega k}{c} x} \cos \omega \left(t - \frac{n x}{c} \right) \\ H_z &= a \sqrt{n^2 + k^2}\, e^{-\frac{\omega k}{c} x} \cos \left[\omega \left(t - \frac{n x}{c} \right) - \psi \right] \end{aligned}$$

where $\psi = \tan^{-1} \frac{k}{n}$. The Poynting vector, averaged in time, is

$$S_x = \overline{\frac{c}{4\pi} E_y H_z} = \frac{c}{8\pi} a^2 n e^{-\frac{2\omega k}{c} x} \quad .$$

This is the radiant power of angular frequency ω crossing unit area as a function of x, the penetration distance into the medium. The power per unit cross section absorbed in a layer dx is thus

$$\begin{aligned} -dS_x &= \frac{2nk\omega}{8\pi} a^2 e^{-\frac{2\omega k}{c} x} dx \\ &= \frac{1}{2} \frac{nNe^2}{m} \frac{\gamma \omega^2 a^2 e^{-\frac{2\omega k}{c} x} dx}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2} \\ &= \frac{4\pi N e^2 \gamma}{mc} \frac{\omega^2 S_x \, dx}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad . \end{aligned}$$

If we illumine the substance with continuous light of constant intensity,

$S_x(\omega_o)d\omega$ being the power per unit area in interval $d\omega$,

$$-dS_x = dx\ \frac{4\pi\mathcal{N}e^2}{mc}\gamma S_x(\omega_o)\int_0^\infty \frac{\omega^2 d\omega}{(\omega_o^2-\omega^2)^2+\gamma^2\omega^2}$$

and by setting $z=\frac{2(\omega-\omega_o)}{\gamma}$, $\omega_o^2-\omega^2\approx-\omega\gamma z$,

$$-dS_x \approx dx\ \frac{2\pi\mathcal{N}e^2}{mc} S_x(\omega_o)\int_{-\infty}^{\infty}\frac{dz}{1+z^2}$$

$$= dx\ \frac{2\pi^2\mathcal{N}e^2}{mc} S_x(\omega_o)\ .$$

Thus the power absorbed per unit volume of medium is

$$-\frac{dS_x}{dx} = \frac{2\pi^2\mathcal{N}e^2}{mc} S_x(\omega_o)$$

$$= \frac{\pi\mathcal{N}e^2}{mc} S_x(\nu)$$

$$= \frac{\pi\mathcal{N}e^2}{m} u_\nu$$

since $u_\nu=\frac{S_x(\nu)}{c}$, and where $S_x(\nu)$ is the power per unit area per unit frequency range ($S_x(\nu)d\nu=S_x(\omega)d\omega$). The same quantity is given by the Einstein phenomenological theory:

$$-\frac{dS_x}{dx} = \mathcal{N} u_\nu B_{ul} h\nu$$

and by comparison we obtain the relation

$$\frac{\pi\mathcal{N}e^2}{m} = \mathcal{N} B_{ul} h\nu$$

And since $f=\mathcal{N}'/N$,

$$f = \frac{mh\nu}{\pi e^2} B_{ul}$$

$$= \frac{mc^3}{8\pi^2 e^2\nu^2}\frac{g_u}{g_l} A_{lu} \qquad (8)$$

from (1).

It should be noticed that N as used above is the number of atoms per unit volume which are active in the absorption process. That is, if the gas is in thermal equilibrium,

$$\mathcal{N} = N_o \frac{g_l}{g_o} e^{-E_l/kT}\ . \qquad (9)$$

The total number of atoms per unit volume of gas is

$$n = \sum_l N_o \frac{g_l}{g_o} e^{-E_l/kT} \qquad (10)$$

where the sum is taken over all the energy levels possible for the atom. If the particular transition is a resonance transition from the ground

state, and if the ground state ($E = 0$) is well separated in energy from the excited states ($E_\ell/kT \gg 1$) then

$$N = N_o \approx n \quad , \tag{11}$$

and essentially all the atoms present are active in the absorption process. Also, in this resonance case, the lifetime of the state, τ, is simply given by

$$\tau = 1/A_{\ell u} \quad . \tag{12}$$

VI. Methods of Measurement of f-values

Although few f-values have been measured, a rather large number of methods have been developed--most of these having been used only on the D lines of Na and the resonance lines of Hg. These methods are summarized by Mitchell and Zemansky[5], and may be grouped in the following rough classifications: 1, emission methods; 2, absorption methods; 3, dispersion methods; 4, methods utilizing magneto-rotation; and 5, depolarization methods.

1, emission methods. These are essentially of two types. The first involves a colimated beam of excited atoms, which consequently emit characteristic resonance radiation. The intensity of this observed radiation falls off exponentially along the beam because of the finite lifetime τ of the excited state. If the velocity of the beam is known, τ may be estimated from intensity measurements.

The second emission method consists of observing the intensities of emission lines from a sample of gas which is in thermal equilibrium at high temperature. These intensities are proportional to the Einstein $A_{\ell u}$, and hence again the f-values may be computed (eq. (12)).

The measurement of intensity in absolute units presents many difficulties, but relative f-values of different transitions of the same atom may be conveniently obtained by this method[6].

2, absorption measurements. If radiation (which may be of a resonance frequency, or continuous) is passed through a confined sample of vapor which is kept at thermal equilibrium in an absorption cell, the resulting absorption lines may be studied in detail: various methods involve measurements of the absorption coefficient at the center of the line, in its wings, and also integrated over the line. The method used in the present investigation was of this general type, where the fractional energy removed from the continuum was determined. It will be discussed in greater detail in the following section.

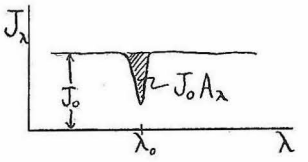
3, methods involving dispersion. In the extreme wings of an absorption line the effects involving an anomalous index of refraction are much more pronounced than the slight absorption that may occur. Measurements of dispersion in the wings (and also of normal dispersion even farther from the line) can again lead to estimates of oscillator strengths (see equation (6)).

Methods 4 and 5 involve the Faraday effect (magneto-rotation), and the absorption and re-emission of resonance radiation (with consequent depolarization) in magnetic fields. We shall not consider them except to remark that, again, only the Na and Hg resonance lines have been investigated, and that some of the observed effects are not in agreement with theory (see Mitchell and Zemansky[5], Chapter V).

VII. The Method of Total Absorption

Consider an optically thin, homogeneous layer of absorbing atoms, of thickness ℓ. If light from a continuous source of intensity $J_{\lambda 0}$ (ergs per second per unit solid angle per unit cross section, in the wave length range between λ and $\lambda+d\lambda$) be passed through the layer and focused on the slit of a spectrograph, the resulting spectrogram will show a continuum of uniform intensity crossed by absorption lines--regions of weaker intensity. By suitable plate calibration, the area under microphotometer tracings of these lines may be measured and interpreted as being proportional to the integrated diminution in across the line, resulting from the absorption of energy from the continuum by the atoms comprising the layer.

If the transmitted intensity J_λ is plotted against λ, we obtain

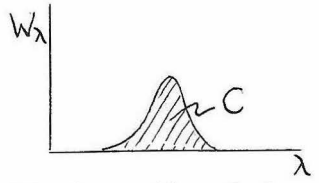


a plot of constant continuum height J_o, showing an absorption line at λ_o, whose area we shall denote by $J_o A_\lambda$. Hence A_λ is the equivalent wave-length interval removed from the continuum by the absorbing layer. It is customarily expressed in Angstrom units, and is called the "equivalent width" or "total absorption" of the line.

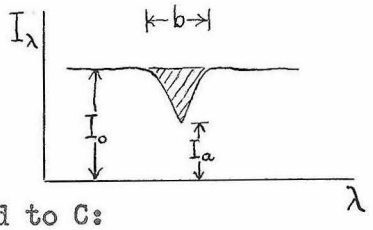
Allowing for the geometry of the optical system and the continuous absorption, scattering, etc., which will have occurred in its elements, the illumination of the slit will have an exactly similar spectral distribution, say KJ_λ.

The "window curve" of the spectrograph is the result of the finite

slit width and the imperfect resolution of the diffraction grating. It may be represented by an amplitude W_λ plotted against λ, since the dispersion of a Rowland mounted grating is linear with distance along the plate. The "window" has an area C in Angstrom units.



The light intensity incident on the photographic plate is the "fold" or convolution of these two curves, and has again the same general characteristics:



I_o is proportional to J_o and to C:

$$I_o = \kappa K J_o C ,$$

and also, since the area under the fold of any two curves is the product of the areas under the separate curves, the observed tracing area is

$$\frac{I_o - I_a}{2} b = \kappa K J_o A_\lambda C .$$

The equivalent width of the line, A_λ, is hence simply given by

$$A_\lambda = \left(1 - \frac{I_a}{I_o}\right)\frac{b}{2} . \qquad (13)$$

It should be noted that A_λ is directly obtainable from microphotometer tracings of the plate, and does not require knowledge of the instrumental window. This is a very convenient feature of the method of total absorption, and has been verified experimentally by Minkowski[7].

If the incident continuous light be practically plane-parallel, let $S_x(\lambda)$ be the incident power per unit cross section in interval $d\lambda$. The energy density in the layer will be S_x/c. Assuming that all the

excited atoms $N\ell$ in the optically thin layer are active in absorption (picturesquely, none of them are shadowed by the others), the energy absorbed per second per unit cross section will be $h\nu N\ell B_{u\ell} u_\nu$. Also $S_x(\lambda)\,d\lambda = c u_\nu\, d\nu$, hence $u_\nu = (\lambda^2/c^2) S_x$. Thus

$$A_\lambda = h\nu N\ell B_{u\ell} \frac{\lambda^2}{c^2} S_x \div S_x$$
$$= \frac{\pi e^2 \lambda^2}{mc^2} N\ell f \qquad (14)$$

from (7).

Equation (14) is of course an approximation based on the assumption of optical thinness. The exact functional dependence of A_λ on $N\ell f$ is the so-called curve of growth (see, e. g., Unsold[8]). For small values of the equivalent width this functional relation is linear as expressed by (14). However with larger equivalent widths the absorbing layer is no longer optically thin for wave-lengths near the center of the line, and the absorption there is almost complete. As a result, the "growth" of the line with increasing $N\ell f$ becomes very slow, being entirely due to the increased absorption in the wings of the line, which have a Gaussian shape due to the so-called Doppler broadening of the line. This latter is due to the thermal motion of the atoms comprising the absorbing layer. For very large values of $N\ell f$, the extreme wings of the line, which result from the natural resonance shape of the line (see equation (7)) and from pressure effects, become of paramount importance, and A_λ then grows as the square root of $N\ell f$. The method of total absorption is applicable with accuracy only on the linear and lower Doppler regions of the curve of growth, where pressure and natural damping effects are absent.

The method of total absorption, then, provides a convenient method of obtaining atomic f-values from measurements of A_λ, which are obtained

directly from microphotometer tracings of the spectrograph plates. For relative f-values, in particular, the method is capable of considerable accuracy. If, in this case, the lines to be compared are all ground state transitions, N_o is the same for all, and the ratios of the f-values are directly obtainable. If some of the lines arise from absorption by atoms in excited states, then care must be taken to maintain thermal equilibrium in the vapor, so that N/N_o may be calculated from (9). The method is also capable of yielding accurate absolute f-values, provided the value of N can be determined.

In the present investigation the vapor was confined in a closed cell, over the solid. Care was taken that conditions of thermal equilibrium were maintained, and hence from (11), $N_o = n = P/kT$. The last equality follows from kinetic theory, where k is Boltzmann's constant, and P is the vapor pressure of the solid at temperature T. P is the weakest link in the entire calculation, as reliable values of the vapor pressure are obtainable for suprisingly few substances, and thermodynamic calculations are unreliable. An estimated error of 20% in reported determinations of vapor pressure is quite common, and 5% error is about the best that can be found for any element[9]. Hence the experimental results of this work will be reported first as the product nf, and then second as f, where this latter is calculated using the best obtainable value of P from the work of other investigators.

VIII. Apparatus and Method

The elements to be studied were introduced into small quartz "pill-boxes", 1 inch in diameter and approximately $\frac{1}{2}$ inch deep. This last dimen-

sion, ℓ , is the length of the column of absorbing vapor, is needed for the reduction of the data, and was obtained by micrometering the end plates of the absorption cell before they were welded onto the cylindrical side wall, and subtracting their thickness from the overall depth of the completed cell. These cells were equipped with a side arm and stopcock, the side arm being somewhat constricted next to the cell so that the cell could be completely sealed off after introduction of the metal to be studied. Each cell was baked out under vacuum and then, argon filled, transferred to a "dry box". The dry box consisted of a sealed plywood cabinet, with glass top, and rubber surgeon's gloves projecting inward with which the contents might be manipulated. Dry He was circulated through the box while the cell was being filled. A cleaned sample of metal was further mechanically cleaned (filed) inside the He atmosphere, and a small amount of filings dropped into the cell. The cell was flushed several times with the He, and then the stopcock was closed. The cell was then removed from the dry box, sealed onto a vacuum system, pumped out to a pressure of less than 1 micron, and sealed off at the constriction.

The electric furnace in which the cell was then placed has been described by King and Stockbarger[10]. The heating elements consisted of two 10 inch concentric Alundum cylinders, wound with .020 inch molybdenum wire. The inner, or main, heating coil was continuously wound, and in practice carried up to 7 amperes of 60 cycle a.c. The outer coil was wound for only about 4 inches on either end, and a center tap connection was made between these two windings; hence independently variable current was possible in each of the two sections of the outer coil. The

heating coils were surrounded by two concentric nickel radiation shields, and nickel shields with 3/8 inch holes were also mounted at either end of the heating coils. The absorption cell was mounted in an Alundum capsule of about 1¼ inch diameter and 2 inch length. The capsule completely surrounded the cell, except for 3/8 inch holes at either end. This capsule was placed exactly in the center of the core of the inner coil, with two identical but empty capsules spaced toward either end of the core serving as axial radiation baffles. A platinum-10% platin-rhodium thermocouple, supported in a 6 inch length of small double-holed ceramic thermocouple tubing, ran through small holes in one of the end capsules and through one end of the center capsule, so that the junction was about 1/8 inch from the end plate of the absorption cell, and about ¼ inch from its axis.

The two Alundum cores and surrounding nickel shields were supported on baked soapstone pieces at either end, and this entire structure bolted to a brass bar which was clamped to the end plate of the furnace. The electrical connections and thermocouple leads all passed through this end plate, so the entire contents of the furnace could be removed merely by unsealing the end plate, clamping it in an exterior wooden supporting cradle, and sliding the cradle directly out and away from the furnace.

The furnace proper is a 6 inch steel pipe, 18 inches in length, permanently closed at one end by a cast-iron cap, and flanged at the other. The end plate fits smoothly against this flange, and is sealed with ordinary laboratory wax pressed into a v-groove around the outer edge. Both the cap and end plate carry water-cooled brass window holders in their centers, and plane quartz windows were waxed onto these. The

body of the furnace is surrounded by a copper water jacket, through which water was circulated vigorously.

For the experiment it was desired to have thermal equilibrium over the central region of the furnace occupied by the cell and the thermocouple juncture. This was insured by running preliminary tests in which a movable thermocouple, controlled magnetically from outside the furnace, tested for the existence of temperature gradients in this central region. It was found that by maintaining a fixed ratio between the currents in the two independent windings of the outer coil, variations in temperature could be minimized to less than $\frac{1}{2}^{\circ}$ C. over a region some $1\frac{1}{2}$ inches in length. At the highest temperatures used in the Ni investigations this ratio was not tested; however the cell and fixed thermocouple together only occupied some 5/8 inches in the center of the core, so both temperature equilibrium and reliable temperature indication by the thermocouple would seem to have been achieved.

The furnace was evacuated to about 50 microns of Hg by a Hypervac mechanical pump. This served to protect the heating coils from the water and oxygen of the air, and also avoided extreme convection currents which might otherwise have disturbed temperature uniformity inside the furnace. The pressure was checked with a McLeod guage.

The main coil required some 200 volts, after becoming heated, to maintain a current approaching 7 amperes. This was delivered by a large 5 kva Variac transformer, through a 2 to 1 step-up transformer. The two outer coils were driven from a $\frac{1}{2}$ kva Variac, and across one of them a variable resistor provided means for varying the ratio of currents in them. A. c. ammeters continuously read the current in each of the three

windings.

The thermocouple weld was made, and the thermocouple calibrated by the National Bureau of Standards, from whom it received the designation III-1d No. 8095. The calibration was guaranteed to less than 0.5° C. from 0° to 1100° C., and to not more than 2° at 1450° C. During actual exposures, which ran as long as 15 minutes, the Variac settings had to be manipulated continually to compensate for slow drifts in temperature. Occassionally these drifts varied by as much as $\frac{1}{2}$° C. on either side of the temperature recorded, though they were held to less for most of the exposure. As a result, an overall probable error of 1° C. has been adopted in the calculations.

The potential of the thermocouple was measured using a 15,000 ohm Wolff potentiometer, a standard Eppley cell which was calibrated by the standards laboratory of the Institute, and a Leeds and Northrup type R galvanometer. The cold juncture of the thermocouple was at room temperature, which was recorded to $\frac{1}{4}$° C. during each exposure. This arrangement gave temperature readings to $\frac{1}{4}$° C.

The continuous light source used for the Ca and Cr investigations was a 1 kw, 30 ampere, 4-coil projection lamp, overloaded to around 33 amperes, operated by a d.c. motor-generator set through an adjustable lamp bank. About 15 minutes exposure of the photographic plate was required to record a continuum of proper density at 4200 Angstroms. For the Ni investigations (at around 3400 Angstroms) a quartz, water-cooled super high pressure Hg arc lamp was used. This lamp is similar in type to the Bol lamp made by Phillips[11], and was constructed by the Huggins

Laboratories, Menlo Park, California. In the spectral region used, 10 minutes exposure gave a continuum of proper density. The continuum was crossed at the Hg lines by regions of greater intensity, which fortunately did not occur close to the Ni lines being investigated.

The light from the lamp first passed through a 60 cm. quartz lens, then through the window in the furnace cap, through the several 3/8 inch holes to a focus approximately at the absorption cell. Because of the long focal distance and the several image stops, the light passing through the cell was very close to parallel. Emerging from the cell, the light again passed through several 3/8 inch stops, through the window in the furnace end plate to a 40 cm. lens which again rendered it slightly convergent. For convenience of physical arrangement the light beam was then deflected by a front surfaced plane mirror, then made more convergent by another 40 cm. quartz lens, and thence to the small quartz collecting prism of the spectrograph. This last made the beam vertical, and the lamp image focused on the spectrograph slit directly below the collecting prism.

The spectrograph used was the 15 foot vertical Rowland spectrograph of the Mount Wilson Observatory. In the second order, this instrument has a dispersion of 1.86 A. per mm. Fine grain, high contrast plates were used, both Eastman IV-O and Cramer Contrast, the Cramer plates being ultimately adopted because of slightly higher speed and greater uniformity of emulsion. These plates, 3 x 10 inches, were cut lengthwise, one half being used for the exposure, the other half for a calibration plate. The two halves were then developed simultaneously in D-19 developer.

The calibration plates were exposed for the same length of time as

the others to the light from a voltage-stabilized quartz Phillips ribbon lamp, using a calibrated step-slit. The step slit had nine graduated widths of known values. Microphotometer tracings of the calibration plates then show nine successive degrees of photographic blackening, plus tracings of clear unexposed glass and of complete blackness.

The microphotometer is that of the Mount Wilson Observatory. It records photographically the intensity falling on a photocell behind a slit upon which is projected a considerably magnified transmission image of the plate. The gearing of the microphotometer was set at 100:1 ; that is, the wave-length scale on the microphotometer tracing is 100 times that on the plate. On all tracings the directly measured quantities were (1) the base width of the line, (2) the fractional darkening of the plate at the continuum and (3) the fractional darkening at the apex of the absorption line. The fractional darkening is the distance on the tracing from the exposure to the clear glass, where the distance from complete blackness to clear glass is taken to be 100.

IX. Reduction of Data

For the tracings of the calibration plates, the fractional darkening was plotted vs. the logarithm of the step slit width. The absolute value of this latter is unimportant, as it is the slope of the resulting curve which is characteristic of the plate, and which is required for the subsequent reduction of data. We shall denote this logarithm of the step slit width (in mm.) by log I . If the conditions under which the plate was exposed are constant, I is then proportional to the intensity of light which fell on the plate, and hence to the quantities I in equation (13).

The absorption lines appeared on the microphotometer tracings as roughly triangular in shape. Because other considerations precluded their being too large (both for accuracy in reading from the curve of growth and to avoid pressure broadening of the lines) they were usually uncomfortably close in magnitude to the natural film density variations due to grain. This meant that no shape other than triangular could be consistently applied, and their areas were calculated on that basis.

On each tracing of a line, three readings were taken. These were r_o , the fractional darkening of the continuum near the line; r_a , the fractional darkening at the apex of the triangular line; and finally b, the width in mm. of the base of the triangle. From the plotted calibration curve for the plate, values of log I_o and log I_a were then read. The antilogarithm of the difference of these is the ratio of the intensity of light transmitted by the cell as the wavelength of the center of the absorption line to that transmitted a few angstroms away where there is no absorption by the vapor. One minus this ratio, multiplied by one-half the base width in angstroms (because the line shape is roughly triangular) is then the equivalent width of the line A_λ expressed in angstroms (see equation (13)).

A large graph was plotted of the expression given by Unsold [8] for the linear and lower Doppler portions of the curve of growth:

$$A_\lambda/\Delta\lambda_D = \sqrt{\pi}\, C\left[1 - \frac{C}{2!\sqrt{2}} + \frac{C^2}{3!\sqrt{3}} - \frac{C^3}{4!\sqrt{4}} + \cdots\right]. \qquad (15)$$

Here $C = k_o N \ell f$, where $k_o = \frac{\sqrt{\pi}\, e^2}{mc^2}\frac{\lambda^2}{\Delta\lambda_D}$. Also $\Delta\lambda_D = \frac{\lambda}{c}\sqrt{\frac{2RT}{M}}$ is the so-called Doppler width of a line from a metal of atomic weight M, at temperature T^o K. R is the gas constant. This relation of course reduces to (14) for $C \ll 1$. From the experimental values of A_λ , C was read directly from

this graph, and hence Nf immediately calculated.

The largest experimental random error is unquestionably that of measuring the triangular areas from the microphotometer tracings. In practice each line was traced at least five times at five slightly differing positions on the plate. Thus the grain "noise" on the five tracings was different in each case. The five ratios I_a/I_o thus measured usually agreed with a mean deviation of 3% or less, and their average was adopted. Considerably larger scatter in the values of the base widths b usually occurred, however. This is undoubtedly due to the grain noise, which makes it difficult to determine where, on any given tracing, the sloping sides of the triangle should be ruled.

On a given plate, taken during a single furnace run, five or six exposures were taken in succession at temperature intervals of about 10° C. All other physical conditions, such as slit width and spectrograph adjustments were kept constant. Any given exposure showed from three to five closely spaced absorption lines, for the elements Ni and Cr investigated. As has been remarked, each of these lines was microphotometered at least five times. As a result, from one plate, some 75-150 measurable traces resulted. The measurements of base width b of all the traces from a given plate showed an unmistakable tendency for the strong lines to have larger widths than the weaker. This increase amounted to around 15% from the weakest measurable (almost disappearing in the plate grain) to the strongest (well up on the lower Doppler portion of the curve of growth). No real physical reason for this has been adduced. The Doppler width for all the lines on a plate (all taken at sensibly the same furnace temperature, at very slightly

differing wave-lengths) and the fixed instrumental broadening should lead to the same base width in every case. It was concluded that the effect was spurious, and due to the confusion by the grain as to where the sides of the triangles were ruled. So all the measured base widths for any given plate were averaged, and this average value of b adopted in the computations of equivalent width for all the lines appearing. This value differed from the extremes by about 7%, indicating a probable error in the measurements of A_λ of about 5%.

The values of Nf of all the lines of a given plate were obtained from the curve of growth and, from (9) and (10) or (11), reduced to values of nf. Comparison of these yields the relative f-values for the several lines studied; and also these nf-values can then be used to determine the constant A for the vapor pressure curve of the substance.

The usual form of the vapor pressure curve for sublimation of a solid is

$$\log P_{mm} = A/T + B \,.$$

This yields

$$\log n = -\log T + A/T + \text{const.}$$

and hence we may set

$$\log nfT = A/T + \text{const.} \qquad (16)$$

Hence from the present data the value of A may be determined from the plot of nfT vs. 1/T. This provides a check, at least, on the vapor pressure data which must be adopted from the work of other investigators to arrive at the final absolute values of the oscillator strengths.

X. Calcium

The abundances of the alkali earths, Mg, Ca, Sr and Ba are of considerable interest astronomically, and the original object of this investigation was to obtain absolute oscillator strengths for some or all of their resonance transitions.

These elements are all characterized by a spectrum of singlet and triplet terms, since they each have two optically active electrons. The transitions which it was proposed to study were those from the ground state $^1S_0$ to the first excited states $^1P_1$ and $^3P_1$. The relative oscillator strengths of these transitions are known in some cases, and lifetime measurements have also led to estimates of absolute f-values[12][13][14]. The vapor pressures of these elements, especially that of Ca[9][15], are known with considerable precision, and hence the determination of absolute f-values by the method of total absorption should be feasible.

One difficulty is that the vapor pressures are inconveniently large! As a result, the work must be done at relatively low temperatures, from 200 to 500° C., in order that the observed equivalent widths remain on the linear and lower-Doppler portions of the curve of growth. These low temperatures in turn mean that the Doppler widths of the lines are small; hence from equation (15) the equivalent widths on the lower portion of the curve of growth are of the order of 10^{-3} A. A line with an equivalent width of 10^{-3} A. is barely detectable on fine grain plates in the second order of the 15 foot spectrograph. One method of improving this situation was to construct the absorption cells with ℓ as small as possible--thus permitting a somewhat larger value of n, and hence allow-

ing the use of a somewhat higher temperature.

The first, and typical, alkali earth to be studied was calcium, both because its vapor pressure was fairly well established, and because its resonance lines lie in the visible spectral region. The cells used were constructed from pyrex glass. The handling of the metal in filling the cells was particularly important, as Ca reacts violently with oxygen, nitrogen and water.

After considerable preparations for the experiment were made, it was discovered that Ca also reacts with both glass and quartz, apparently reducing the Si in them, which appears as a brownish-black opaque stain on the inside of the cell. This reaction, which occurred at about 450° C.--just under the required temperature range--meant that the experiment was unsuccessful for two reasons. First, the existence of such a reaction indicates a transfer of atoms occurring in the tube between the solid Ca and the walls, and hence that a true equilibrium vapor pressure has not been achieved (the vapor pressure measurements on Ca were taken with the vapor confined in a non-reacting iron tube); and second, the rapid darkening of the tube walls precluded the satisfactory exposure of the spectrograph plate. On only one exposure taken was a Ca resonance line barely visible, and this plate, which required a 30 minute exposure, was badly underexposed!

Several of the absorption cells used were at first heated higher than 500° C. without darkening occurring. These cells also showed no absorption lines. When, however, the temperatures were raised even higher, opacity suddenly occurred. This phenomenon was ascribed to surface impurities on the solid Ca which initially hindered its evaporation.

At the suggestion of Professor W. R. Smythe, the inside surfaces of the windows of several tubes were vacuum coated with CaF_2 by Mr. D. O. Hendrix of the Mount Wilson Observatory before the cells were constructed and filled. It was hoped that this coating would isolate the Ca vapor from the glass walls and prevent the darkening reaction. In most cases this coating had no noticeable effect on the darkening, but in several an annular ring around the outer edge of the coated window remained clearer than the rest of the window and the side wall of the cell. This was thought possibly to be due to the local searing of the coating in this region when the coated window was welded to the cylindrical side wall. Therefore several coated windows were then heated uniformly, and in one case actually melted on a graphite form, before the welding. However, these cells gave no better results than uncoated ones.

On one cell the darkening appeared to have spread upward from the solid Ca, and the possibility was considered that the reaction was not primarily with the vapor, but rather a spreading over the surface of the glass from the solid Ca. To test this a cell with a small side arm or appendix was constructed, and the Ca dust confined in the appendix. On heating, the appendix was completely darkened--the windows remained clear--but no absorption lines were observable. This was interpreted as evidence that an equilibrium distribution of vapor was not attained--the atoms reacting with the walls and not re-evaporating into the vapor phase.

The conclusion reached from these investigations was that the present method of total absorption is inapplicable to these highly active

substances. Two alternatives which might offer more promise are: first, the measurement of the total absorption of a beam of Ca atoms, if the density of atoms in the beam could be determined. The present method depends on the establishment of an equilibrium vapor pressure to determine this density, and this equilibrium is upset by any reactions taking place that involve a unidirectional transfer of atoms. Second, if a convenient method could be developed to seal non-reactive windows (of, say, CaF_2) onto iron tubes, the equilibrium pressure method might again be employed. The results of Brice[16] indicate that this latter possibility is somewhat unlikely.

XI. Chromium

Experimental work has been done on the vapor pressure of chromium by Baur and Brunner[17], and an extensive catalog of relative f-values for Cr transitions is being obtained from electric resistance furnace measurements by Mr. Armin Hill of the California Institute of Technology. Therefore absolute determination of oscillator strengths for a few Cr transitions should be possible and these would be of value in reducing Hill's catalog to an absolute base.

Chromium has a strong resonance triplet in the visible which was easily and consistently observable in absorption at temperatures around 1150° C. These three transitions are a^7S_3-$z^7P^o_{2,3,4}$, whose wave-lengths are respectively 4290, 4275 and 4254 A. The statistical weights of the upper states of this triplet are respectively 5, 7, and 9, and that of the ground state 7.

The chromium was confined in a quartz absorption cell because of

the high temperature required. A small amount of distillation of Cr to the cell walls was noticeable after repeated heatings, but no other change appeared to occur, and the results were reproducible within the limits of random error.

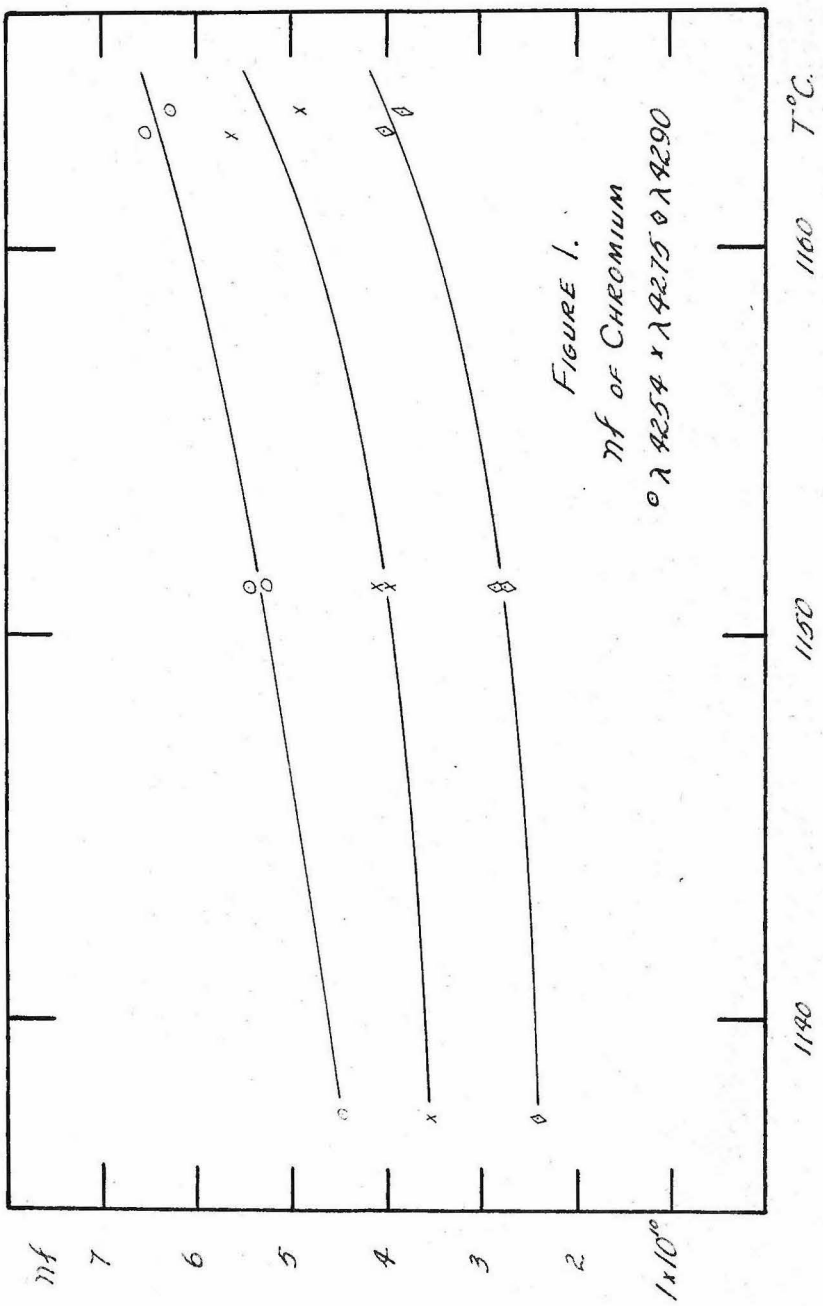
The results to be reported were all derived from one plate, taken during one furnace run. This plate carries five exposures, at temperatures ranging from $1137\frac{1}{2}^{\circ}$ C. to 1164° C. Each exposure shows the Cr triplet, and each of these 15 recorded lines was microphotometered five times. The relative f-values were computed at each temperature. These had about a 3% average deviation from exposure to exposure. Their averages were in the ratio .56:.79:1.00 , which is within two percent of the 5:7:9 ratio of their statistical weights. This ratio is also confirmed by the work of Hill.

The ground state of Cr is simple, and well separated from the first excited state, hence from equation (11) $N \equiv n$. As a result, values of nf were obtained directly from the curve of growth and are shown plotted vs. T in Figure 1. The general trend of the curves for the three lines shows the increase of vapor pressure with temperature, and the scatter of points is indicative of the random errors.

In Figure 2, the quantity nfT is plotted vs. 1/T. Fairly straight parallel lines for the three transitions (corresponding to three different values of f) result, and their slope may be read from the curve. This is A, from equation (16), and for it we thus obtain the experimental value -14000° K.

The vapor pressure equation arrived at by Baur and Brunner[17] is

$$\log P_{mm} = -\frac{10220}{T} + 6.491 \quad ,$$


mf
7
6
5
4
3
2
1×10⁶
1140
1150
1160
T°C.
FIGURE 1.
mf OF CHROMIUM
○ λ 4254 × λ 4275 ◇ λ 4290

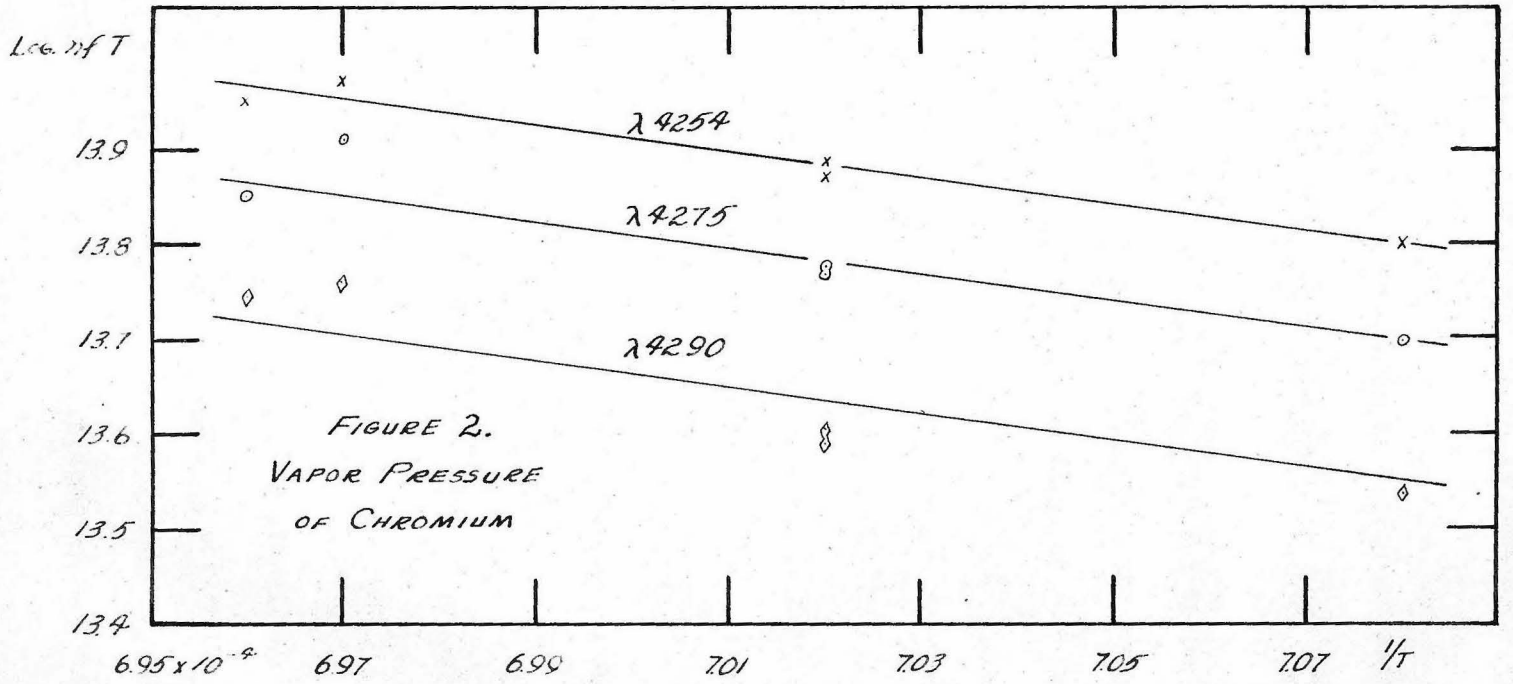


FIGURE 2.
VAPOR PRESSURE
OF CHROMIUM

while if the expression semi-theoretically derived by Kelley[15] is plotted for this temperature range, it is seen to correspond roughly to a value of A = -20000. Hence the temperature dependence of n according both to Baur and Brunner and to Kelley is incompatible with the present data.

There is, furthermore, a large difference in the order of magnitude of n as computed from these two sources. At 1150° C. Baur and Brunner measured a pressure corresponding to n of the order of 10^{15} atoms/cc., while calculations based on Kelley's work give n to be of the order of 10^{12} atoms/cc. Thus, if Baur and Brunner's data were adopted, the f-values for these strong resonance transitions would be of the order of 10^{-5}, which is impossibly small.

It was concluded that the data of Baur and Brunner are incorrect, and, for lack of better, the absolute f-values for the three transitions tentatively calculated using the vapor pressure expressions given by Kelley. The results of this calculation are shown in Figure 3. The horizontal lines in that figure are drawn through the <u>average</u> f-values so calculated. These are: f(4290) = .0068 , f(4275) = .0097 , and f(4254) = .0122 . Their relative values are within 2% of 5:7:9. Systematic deviations of the points at the lowest temperature again emphasize that the experimental A from this spectroscopic work is not in agreement with that derived by Kelley.

These absolute f's, then, partake of only a provisional validity because of the uncertainty as to the vapor pressure of chromium. The values of nf, which are good to a probable error of around 7%, can be reduced to absolute f-values when further work is done on the vapor

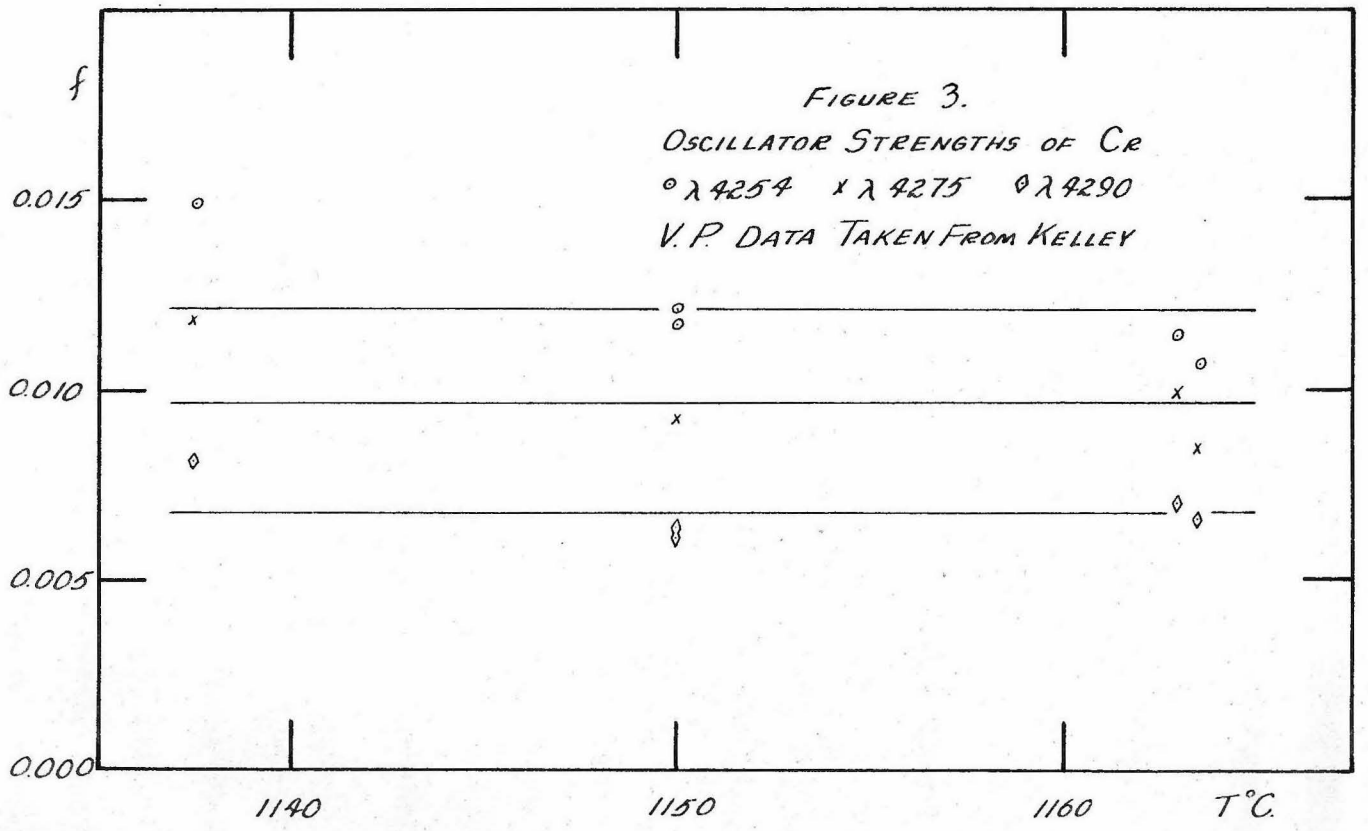


FIGURE 3.
OSCILLATOR STRENGTHS OF Cr
°λ4254 xλ4275 ◊λ4290
V.P. DATA TAKEN FROM KELLEY

pressure. These are reported in Table 1 and plotted in Figure 1.

XII. Nickel

The relative gf-values for some 134 lines in the near ultra-violet spectrum of Ni have been reported by R. B. King[18], who also includes for comparison on the same relative scale some 50 measurements of arc emission intensities by H. van Driel[19]. Rather large deviations occur between the two, which King remarks are probably due to his inherently less accurate absorption measurements. On the other hand van Driel's arc measurements are open to serious question because of the probable occurrence of self-reversal--this latter being almost inescapable in the case of strong resonance lines observed in emission.

The vapor pressure of Ni has been calculated by Kelley, principally on the basis of work by Jones, Langmuir and Mackay[20]. More recently, the vapor pressure has been redetermined by Johnston and Marshall[21], whose values of n (near 1300° C.) are about 2/5 those of Kelley. The work of Johnston and Marshall was done in the General Electric laboratories, agrees well with the original data of Jones, Langmuir and Mackay, and appears very reliable. They estimate their error at no more than 5%.

The nickel used in the present work was electrolytically purified, and showed no traces of impurities in an arc spectrum. In the absorption spectrum, however, where the metal was confined in a quartz cell, the resonance absorption lines of both Na and Ag were detectable. The vapor pressures of both these elements are quite high, and the fairly weak absorption lines which they gave at around 1300° C. showed that they were

TABLE 1

	1437	1436	1423	1423	1410.5° K.
λ 4290	3.86×10^{10}	4.05×10^{10}	2.74×10^{10}	2.84×10^{10}	2.42×10^{10}
λ 4275	4.93	5.67	4.14	4.02	3.53
λ 4254	6.28	6.55	5.26	5.40	4.47

present in sub-microscopic amounts, which would not influence the vapor pressure of the Ni. It is of interest to note, however, that absorption spectra from confined samples thus seem to be an even more delicate test for sub-microscopic amounts of volatile impurities than the more customary arc emission spectra.

At the elevated temperatures used for the nickel measurements, some difficulty was had with the quartz absorption cells. The quartz devitrified, and became milky after one or two heatings. Even on the best plates obtained, the density of the continuum was noticeably lighter on the later exposures.

The thin side walls of the nickel-filled cells also tended to expand plastically at these high temperatures. One cell became almost spherical when heated to around 1360° C. The f-values obtained from this run, which included six exposures starting at 1319° C. and ending at 1255° C., appeared to decrease uniformly with with temperature to a value almost half the original (hence, increase with time to value twice that first obtained). This was apparently because the data was reduced on the assumption of a constant path length, while the path length actually increased as the cell expanded. All data from this cell were discarded.

The reason for such a high internal pressure in the cell (the furnace proper was only evacuated to around 50 microns) was probably a very slow leak, which allowed some air to be trapped in the cell between heatings. Fortunately the presence of non-reacting gasses has no influence on equivalent widths on the linear and lower-Doppler portions of the curve of growth. The last cell used, from which the data to be presented was obtained, was not taken higher than 1310° C., and while it became somewhat

milky, it did not swell appreciably.

The three Ni lines which were investigated arose from the transitions $a^3D_3-z^5F_4^o$ λ3461.7 , $a^3D_3-z^3P_4^o$ λ3524.5 , $a^3D_3-z^3F_4^o$ λ3414.8 . The statistical weight of the lower state of these three lines is 7. Two other Ni lines appeared very faintly on the exposures taken at the highest temperature. These arose from the transitions $a^3D_3-z^3D_3^o$ λ3393.0 and $a^3F_4-z^3D_3^o$ λ3369.6 .

Nickel does not possess a simple, well isolated ground state. It has, rather, some seven closely spaced low levels, over which a summation must be taken and introduced into equations (9) and (10) to compute the fractional population of a state such as a^3D_3. These low-lying levels, together with their excitation energies expressed in wave numbers are given in Table 2. For example, at 1282° C., (9) and (10) lead to $N = .2821\ n$ for the state a^3D_3.

TABLE 2

a^3F_4	0.00 cm.$^{-1}$
a^3F_3	1332.15
a^3F_2	2216.55
a^3D_3	204.82
a^3D_2	879.82
a^3D_1	1713.11
a^1D_2	3409.95

The nickel data that were obtained agreed with the vapor pressure curve given by Johnston and Marshall. The results from one plate are

shown in Figure 4, in which f is plotted vs. T for the three observed lines. The horizontal lines shown in this figure represent the average f-values derived. These are: $f(3461.7) = .0093$, $f(3524.5) = .0183$, and $f(3414.8) = .0171$. The overall probable error for these f-values, considering the 5% probable error reported by Johnston and Marshall for their vapor pressure data, is something like 10%.

King reports relative gf-values for these three lines of 2400, 5500 and 4500 respectively, while he gives the relative gf-values of van Driel on the same scale to be 3560, 5810 and 5270. A least square fit of the new absolute values to the relative values of King for these three lines results in the conversion factor $2.55 \times 10^{-5} \pm .12 \times 10^{-5}$. This number, multiplied by any one of the relative gf-values of King's table, should then give the corresponding absolute gf-value.

The three experimental absolute f-values derived in the present work, multiplied by 7 (g for a^3D_3) and divided by 2.55×10^{-5} , give respectivly 2550, 5020 and 4690 as the new relative gf-values on King's arbitrary scale. These compare well with King's previous results, and differ considerably and systematically from those of van Driel.

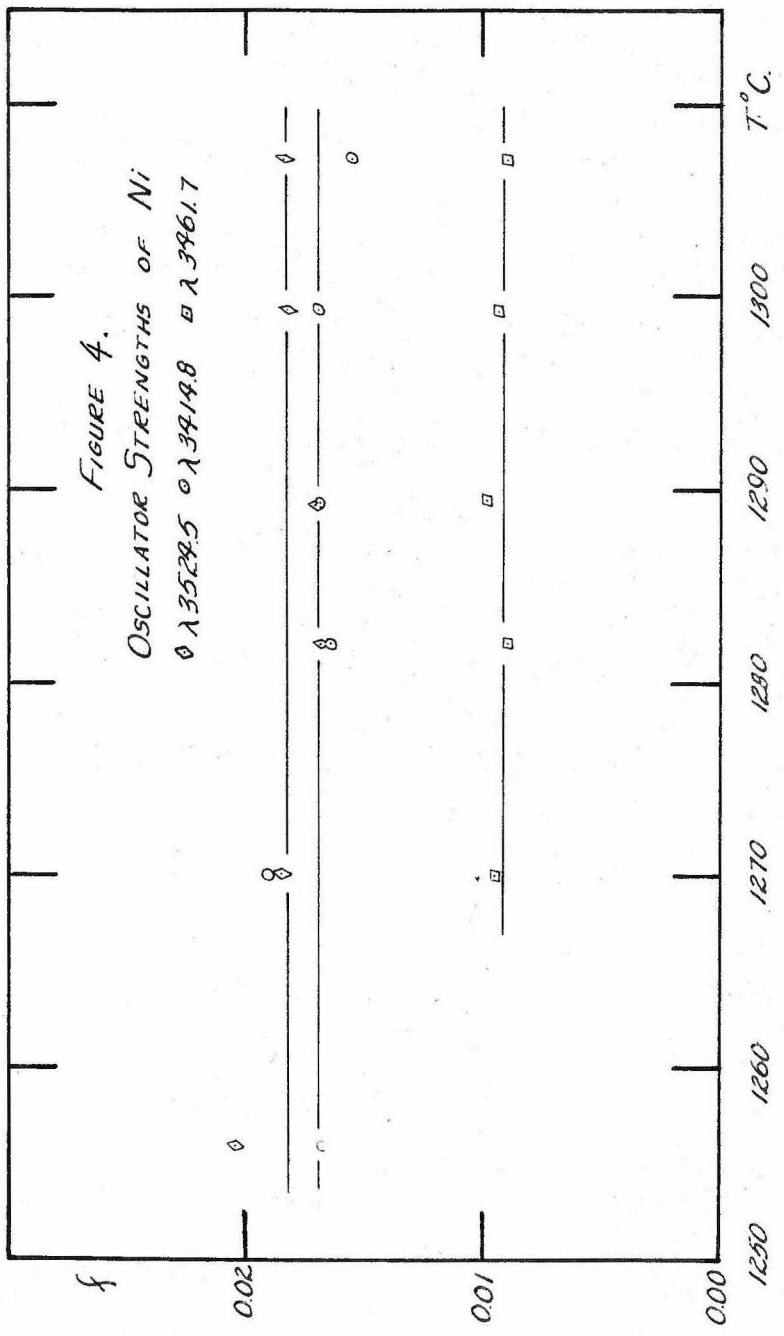


FIGURE 4.
OSCILLATOR STRENGTHS OF Ni
◊ λ 3524.5 ○ λ 3414.8 ▫ λ 3461.7
f
0.02
0.01
0.00
1250
1260
1270
1280
1290
1300
T.°C.

XIII. References

1. Most of the theoretical computations are referred to, and results compared, by Bates and Damgaard, Phil. Trans. Roy. Soc. Lond. A No. 842 242 (1949)
2. See, e. g., R. Ladenburg, Zeits. f. Phys. 4 451(1921)
3. H. Bethe, Handbuch der Physik, Vol. XXIV, part 1 (J. Springer, Berlin)(1933)
4. R. Becker, Theorie der Elektrizität, Bd. 2 (Teubner)(1933)
   S. A. Korff and G. Breit, Rev. Mod. Phys. 4 471 (1932)
5. Mitchell and Zemansky, Resonance Radiation and Excited Atoms Chapter III (Cambridge)(1934)
6. W. W. Carter, Thesis (California Institute of Technology)(1949)
7. R. Minkowski, Zeits. f. Phys. 36 839 (1926)
8. A. Unsold, Physik der Sterneatmosphären (J. Springer, Berlin)(1938)
9. Ditchburn and Gilmour, Rev. Mod. Phys. 13 310 (1941)
10. R. B. King and Donald C. Stockbarger, Contr. from Mt. Wilson Obs. No. 629, Ap. J. 91 (1940)
11. C. Bol, Das Licht 5 84 (1935) ; Ingenieur 50 91 (1935)
12. W. Prokofjew, Zeits. f. Phys. 50 701 (1928)
13. J. G. Frayne, Phys. Rev. 34 590 (1929)
14. P. Soleillet, C. R. 194 783 (1932)
15. K. K. Kelley, Contributions to the Data on Theoretical Metallurgy III, Bulletin 383 U. S. Bureau of Mines (1935)
16. R. T. Brice, Thesis (California Institute of Technology)(1936)
17. E. Baur and R. Brunner, Helv. Chim. Acta 17 958 (1934)

18. Robert B. King, Contr. from Mt. Wilson Obs. No. 746, Ap. J. 108 87 (1948)

19. H. van Driel, Thesis (University of Utrecht)(1935)

20. Jones, Langmuir and Mackay, Phys. Rev. 30 201 (1927)

21. Johnston and Marshall, J. A. C. S. 62 1382 (1946)